SIMULATION OF REACTIVE DISTILLATION COLUMN FOR n-BUTYL ACRYLATE PRODUCTION FROM DILUTE ACRYLIC ACID

JESSLYN TAN KIM EAN

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ABSTRACT

The recovery of dilute acrylic acid from the wastewater stream during the production of acrylic esters in the industries has gained a significant amount of attention due to its economic and environment issues. The amounts of acrylic acid which are usually found to contain in the wastewater stream range from 4-10 % w/w. The most frequent used method to treat wastewater containing acrylic acid is by incineration which is neither economically feasible nor environment friendly. One of the promising methods is recovery of acrylic acid from wastewater through esterification. Acrylic acid could be converted to acrylic ester while wastewater could be purified. To date, study about esterification by using diluted acrylic acid has not been reported in the literature.

In this present work, a simulation study on the direct utilization of dilute acrylic acid in the production of n-butyl acrylate via esterification with n-butanol in a reactive distillation column was presented. The reaction is heterogeneously catalyzed by ion exchanged resin (Amberlyst-46). A pseudo-homogeneous kinetic model was used to describe the reaction kinetics. An equilibrium stage model was applied and the proposed model was validated with experimental data from past research study. The validated model was then used to study effect of various parameters like acrylic acid concentration, catalyst loading, reboiler duty, reflux ratio, number of trays in reactive section and number of trays in separation section. From this study, it can be seen that the best operating conditions in recovering 4% w/w acrylic acid from the wastewater stream were with a catalyst loading of 0.105 kg/m, reboiler duty of 283.133 kJ/hr, reflux ratio of 1.0 and finally with 7 trays in the reactive section and 2 trays in the rectifying and stripping section respectively. With these operating conditions, 95.245 % of AA managed to be converted into BA. The findings have proven the feasibility of the acrylic acid recovery via esterification in reactive distillation column and it serves as the groundwork for the detailed column design and experimental study in the future.

ABSTRAK

Pemulihan asid akrilik cair dari aliram air sisa semasa pengeluaran ester akrilik dalam industry telah mendapat sejumlah besar perhatian kerana isu-isu ekonomi dan alam sekitar. Jumlah asid akrilik yang biasanya didapati di dalam aliran air sisa adalah dalam lingkungan 4-10 % w/w. Kaedah yang paling kerap digunakan untuk merawat air sisa yang mengandungi asid akrilik adalah dengan kaedah pembakaran yang tidak digalakkan disebabkan oleh isu-isu ekonomi dan alam sekitar. Oleh itu, salah satu kaedah yang digalakkan untuk pemulihan asid akrilik daripada air sisa adalah melalui pengesteran.Asid akrilik boleh ditukar kepada ester akrilik manakala air sisa boleh disucikan.Setakat ini, kajian mengenai pengesteran dengan meggunakan asid akrilik dicairkan tidak pernah dilaporkan dalam kesusasteraan.

Bagi karya semasa, kajian simulasi kepada penggunaan secara langsung asid akrilik yang telah dicairkan dalam pengeluaran n-butil akrilat melalui pengesteran dengan n-butanol dalam kolum penyulingan reaktif telah dibentangkan. Selain itu, tindak balas adalah heterogen dimangkinkan oleh ion pertukaran resin (Amberlyst-46). Model kinetic berdasarkan kaedah Langmuir-Hinshelwood-Hougen-Watson (LHHW) telah diperolehi dan pemalar kinetic pendekatan ini dan model pseudohomogeneous telah digunakan. Satu model peringkat keseimbangan telah digunakan dan model yang dicadangkan telah disahkan dengan data eksperimen daripada kajian penyelidikan yang lepas.Selanjut itu, model yang telah disahkan digunakan untuk mengkaji kesan pelbagai parameter seperti kepekatan asid akrilik, pemangkin muatan, tugas pengulang didih, nisbah refluks, bilangan dulang dalam seksyen reaktif dan bilangan dulang dalam seksyen pemisahan. Daripada kajian ini, ia boleh dilihat bahawa keadaan operasi terbaik dalam memulihkan 4 % w/w asid akrilik dari aliran air sisa adalah dengan beban mangkin 0.105 kg/m, duti pengulang didih daripada 283.133 kJ/ jam, nisbah refluks 1.0 dan akhirnya dengan 7 dulang di bahagian reaktif and 2 dulang di bahagian membetulkan dan pelucutan masing-masing. Dengan keadaan operasi ini, 95.245 % AA berjaya ditukar menjadi BA. Hasil kajian ini telah membuktikan kebolehlaksanaan pemulihan asid akrilik melalui pengesteran dalam ruangan penyulingan reaktif dan ia berfungsi sebagai asas untuk reka bentuk ruang terperinci dan kajian eksperimen pada masa hadapan.

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SYMBOL	DEFINITION
a_i	activity of component *i* (mol/mol)
C_{act}	concentration of active sites (mol/kg^3)
C_i	concentration of component *i* (kmol/L)
E_a	activation energy (J/mol)
γ	activity coefficient
K_a	activity-based kinetic constant
k	rate constant for pseudo homogeneous model
k_o	pre-exponential factor in Arrhenius equation
K_{eq}	equilibrium constant
$m_{cat,dry}$	mass of dry catalyst per meter packing height (kg/m)
$\dot{n}_i$	mole flow rate of flow *i* (kg/hr)
R	ideal gas constant (J/ (mol K))
r_i	reaction rate of component *i* (mol/s)
T	temperature (K)
v_i	stoichiometric coefficient

LIST OF ABBREVIATION

AA	acrylic acid
BuOH	n-butanol
BA	n-butyl acrylate
CSTR	continuous stirred-tank reactor
EQ	equilibrium model
ER	Eley-Rideal
HETP	height equivalent of a theoretical plate
H_2O	water
LH	Langmuir-Hinshelwood
LHHW	Langmuir-Hinshelwood-Hougen-Watson
LLE	liquid-liquid equilibrium
MTBE	methyl tertiary butyl ether
NEQ	non-equilibrium model
NRTL	non-random two-liquid model
PH	pseudo homogeneous model
RD	reactive distillation
RDC	reactive distillation column
RR	reflux ratio
SAT	super absorbent polymer
UNIFAC	UNIQUAC Functional-group Activity Coefficient model
UNIQUAC	UNIversal QUAsiChemical model
VLE	vapour-liquid equilibrium
WAO	wet air oxidation

1 INTRODUCTION

1.1 Background of study and motivation

Acrylic acid (AA) and its derivatives as the basic building block in the chemical synthesis process have received overwhelming demands for the last few years (Bell, 2003). This in turn has caused the overall production of AA to rise from 3.4 million tons per year to 4.7 million tons per year from year 2003 until 2006 (Glauser *et al.*, 2007). It was reported that the global capacity demand of AA for second quarter of 2011 reached 5.32 million ton per year to cater the demand from United States, Europe, Japan and China. AA is mainly used for producing super absorbent polymer (SAT) which mainly used in baby diapers, adult protective underwear and sanitary napkins (ResearchInChina, 2012; IHS Inc., 2011).

One of the important derivatives of AA is n-Butyl Acrylate (BA), which values at about 30% of the global demand of AA according to Nexant Inc. (2006). It is widely used in the industry as a precursor for varnishes, adhesives and finishes of textiles and papers (Zeng *et al.*, 2006; Altiokka and Ödeş, 2009). Other derivatives of AA and its applications are shown in Table 1.1.

AA possesses harmful properties which could lead to health complication in living species. According to the Dow Chemical Company (2010), AA is corrosive and toxic if absorbed through the skin or inhaled. It is a strong irritant to the skins, eyes and mucous membranes in humans. Possible blindness may occur if its liquids were splashed into eyes. In a typical AA production plant, the wastewater contains 4-10% w/w of AA (Kumar *et al.*, 2010). Some other toxicant of AA family besides AA such as acrylonitrile and acetonitrile are also present in the wastewater stream which is mostly being incinerated due to its high chemical oxygen demand and total organic content. This method suffers from several drawbacks because it is neither economic feasible nor environmental friendly.

Table 1.1: Derivatives of AA and its applications (BASF> Products & Industries> Product finder > acrylic acid, 2013).

Acrylate Ester	Application
Allyl Methacrylate	Mainly used for hydrosilylation of Acrylics and as a cross linking monomer.
Butyl Acrylate	As a building block for homo- and copolymers.
Tert-Butyl Acrylate	Used in several applications, e.g. coatings, adhesives, personal care and plastics.
Tert-Butyl Methacrylate	As a co-monomer in resins for low VOC clear coats, e.g. in car refinish applications.
Tert-ButylaminoethylMethacry	Used for cationic polymers. Main application is in personal care and hair care products.
Ethyl Acrylate	Used as a building block for homo- and copolymers.
2-Ethylhexyl Acrylate	Used as a building block for homo- and copolymers.
2-Hydroxyethyl Acrylate	Used in acrylics for coatings, adhesives and UV reactive oligomers, cross linking with isocyantes or melamines.
Isobutyl Acrylate	Used in coatings, adhesives and PE plastics.
Lauryl Acrylate	Used in coatings, adhesives, plastics and textile applications.

Until today, several treatment methods have been explored which include adsorption through activated carbon, biological and wet air oxidation (Kumar *et al.,* 2010; Lin *et al.,* 1996). This also includes the conventional physical separation methods such as azeotropic distillation, simple distillation and liquid-liquid extraction (Saha *et al.,* 2000). However, these methods present some downfalls whereby adsorption is only practical for low concentration of AA, long retention time is needed for biological treatment and wet air oxidation requires high energy consumption which leads to high operating cost. In view of this, alternative methods of recovering AA have been explored. Recovery of AA from the dilute aqueous wastewater stream through esterification process in a reactive distillation column (RDC) has been identified as a potential important solution (Arpornwichanop *et al.,* 2008). This method would be favour as higher valued esters can be produced through the recovery of dilute AA in a

RDC which in turn would overcome the economic and environmental issue (Taylor and Krishna, 2000).

1.2 Statement of problem

Esterification of AA with alcohols is an equilibrium limited reaction catalyzed by acidic catalyst. To date, RDC is one of the best known examples of process intensification particularly for the equilibrium limited reaction. In an RDC, both the chemical reaction and separation by distillation is combined in one unit operation which is able to drive the reaction to the product site due to *in situ* separation of products (Taylor and Krishna, 2000). RDC has shown its potential for capital productivity improvements, selectivity improvements, reduced energy use and the reduction or elimination of solvents in the process (Malone and Doherty, 2000). Thus, it decreases the amount of equipment required which in turn will results in the reduction in terms of operating cost and investment. As a result, the combination of reaction and separation by distillation assist in overcoming limitations of both operations, such as azeotropes or reaction equilibria.

Currently, the production of acrylate ester is catalyzed by homogeneous catalyst such as sulphuric acid, hydrofluoric acid and para-toluenesulfonic acid (Altiokka and Çitak, 2003). The reaction is carried out in two reactors while the separation of acrylate ester and the recovery of the reactants require a train of three distillation columns after the reactors (Bell, 2003).

However, there are several drawbacks for the homogeneous catalysis system. According to Altiokka and Çitak (2003), homogeneous catalyst is toxic and corrosive towards the environment, it is hard to be removed from the reaction mixture and it causes the purity of the products to be lower compare to heterogeneous catalyst. Since then, heterogeneous catalyst such as solid acid ion exchange resin, zeolite, metal oxides and enzymes has been developed to be applied in the esterification process as solid acid is less toxic towards the environment and it facilitates the recovery and recycling of catalysts (Altiokka and Çitak, 2003; Okuhara *et al.*, 1998; Marchetti and Errazu, 2008; Kiss *et al.*, 2008).

Experimental investigations on the reaction kinetics and the chemical equilibrium of the heterogeneously catalyzed esterification of AA and n-butanol

(BuOH) were investigated in the previous work (Schwarzer and Hoffmann, 2002). To the best of our knowledge, RDC is not practiced for the recovery of AA from diluted aqueous wastewater and only a few publications on the production of BA in a RDC can be found in the literature (Niesbach *et al.*, 2012; Niesbach *et al.*, 2013).

In the present study, AA will be recovered by esterification of wastewater containing AA with BuOH catalyzed by heterogeneous catalyst, ion-exchange resin in a RDC. Since the presence of water in the reactant could reduce the equilibrium conversion due to the shift of reaction equilibrium to the reactant side, efficiency of the AA recovery will be examined in a reactive distillation column (RDC) through simulation study.

1.3 Objectives

This study aims to examine the efficiency of recovering AA from the wastewater containing AA. The effects of important operating parameters for the esterification of diluted AA with Butanol (BuOH) in RDC are investigated.

1.4 Scope of study

In this research, the suitable RDC models (equilibrium or non-equilibrium model), thermodynamics models (UNIFAC, UNIQUAC or NRTL) and reaction kinetics (Langmuir-Hinshelwood-Hougen-Watson, Eley-Rideal or pseudo-homogeneous) were screened before it is employed for the simulation studies. The verification for the simulation on the RDC was carried out by comparing with pilot scale data from past research. Several operating parameters such as acrylic acid concentration, catalyst loading, reflux ratio, reboiler duty and column configuration were varied during the simulation using the validated model.

1.5 Organisation of thesis

This thesis consists of 5 chapters. Chapter 1 (Introduction) provides a description on the application of acrylic acid (AA) and its derivatives in the chemical industries and the effect of its harmful properties. The conventional methods of recovering AA from the dilute aqueous wastewater are briefly described. This chapter includes the problem statements which lead to the identification of the objectives and scopes for the present study. Finally, the organization of thesis is presented.

Chapter 2 (Literature review) describes in details the conventional methods which have been applied in the recovery of AA from wastewater. Besides that, different types of esterification process and catalysts that have been investigated by past researches are also review in this chapter. Information concerning with the implementation of reactive distillation technology for the production of different types of carboxylic acid esters which were review from past researches have also lead to the consideration of catalysts, thermodynamics, modelling and simulation for the reactive distillation(RD) implementation for the current study.

The modelling and simulation procedure is illustrated in detail in Chapter 3 (Methodology). It gives a review on the procedures involved during the simulation of RDC using ASPEN PLUS V7.0 software. The selection of the suitable RD model, thermodynamics model and kinetics model are also being described in this chapter.

Chapter 4 (Results and discussion) is devoted to the simulation results obtained and discussion of the present study. Validation of the RD model for this present study is carried out by comparing with experimental results from past research papers which can be found in the literature. Besides that, the suitable ranges of operating parameters for the recovery of AA in RDC are also being determined after the model has been validated.

Chapter 5 (Conclusion and recommendation) focuses on the conclusion that can be made by the end of the study after analysis the simulation results. The best operating conditions for the recovery of dilute AA in RDC are also presented in this chapter. Lastly, several recommendations are presented in this chapter in order to be considered in future studies.

2 LITERATURE REVIEW

2.1 Overview

This chapter reviewed on the available technology in recovering carboxylic acid from diluted aqueous wastewater streams in today's world. It also describes the recovery of carboxylic acid through esterification process which has been carried out in RDC by past researchers. Besides that, the different types of process which have been investigated through RDC and hardware selections in modelling RDC are also being reviewed in the later parts of this chapter. Finally, a review on the types of RD, thermodynamic and kinetic models which have been investigated in the past for the modelling and simulation of RDC is presented in the final part of this chapter.

2.2 Introduction

Acrylic Acid (AA) is very toxic to living species and it appears as an unsaturated organic acid. During the manufacture of acrylic esters, acrylic acid is being released to the environment. It have been reported that in a typical AA plant, the concentration of AA range from 10-20 g/l in the wastewater stream (Kumar *et al.,* 2008). Thus, the recovery of dilute acrylic acid from the wastewater stream has become very important due to its economical and environmental awareness.

2.3 Wastewater treatment technology for carboxylic acid recovery

According to Cheremisinoff (2002, p.1), wastewater treatment technology can be divided into three areas: Physical Methods, Chemical Methods and Energy Intensive Methods. Physical methods for wastewater treatment are mainly represented by solid-liquid separation techniques. Filtration plays an important role in solid-liquid separation techniques as it is an integral component of wastewater treatment application. In understanding the role of filtration, it is important to make distinctions not only with other technologies applied in the purification of industrial water, but also includes the objectives of different unit processes.

Besides that, chemical methods for wastewater treatment depend upon the chemical reaction of the contaminants to be recovered from the water. It is applied as a

stand-alone technologies as well as an integral part of the treatment process with physical methods.

Moreover, as for energy intensive technologies, the thermal methods have gained much attention due to its dual role in wastewater treatment applications. They can be utilized as a mean of sterilization or utilized to the processing of solid wastes or sludge. In the latter cases, thermal methods can also be applied to sterilize sludge contaminated with organic contaminants.

Several methods have been explored in recovering carboxylic acids from wastewater. In the past, the conventional method includes adsorption through activated carbon (Kumar *et al.,* 2010) and distillation and extraction (Arpornwichanop *et al.,* 2008). However, distillation approach requires high energy usage in vaporizing the water present whereas, extraction is limited by the phase separation and distribution of the component (Saha *et al.,* 2000). As for adsorption through activated carbon, it only deals with chemical wastewater with a low concentration of organic compounds (Kumar *et al.,* 2010). Wet air oxidation (WAO) treatment has also been explored as an alternative method. Due to the high energy consumption which leads to high operation cost, this method is not being favoured (Lin *et al.,* 1996).

Thus, reactive distillation has been introduced as a method in recovering acrylic acid from its dilute aqueous solution. It applies the concept of using the recovered acrylic acid as the reactant for esterification. According to Arpornwichanop *et al.* (2008), this approach is able to produce a higher valued ester, which could save raw material cost and environment issues. Table 2.1 shows the several methods for the recovery of carboxylic acids that have been investigated by past investigators.

Table 2.1: Methods which have been applied for the recovery of carboxylic acids.

Method	**Reference**	**Remarks**
Adsorption through activated carbon	Kumar *et al.* (2010)	Deals only with low concentration of organic compounds (50-500 mg/l) due to long residence time.

Method	Reference	Remarks
Distillation	Saha *et al.* (2000); Arpronwichanop *et al.* (2008)	Unable to achieve high conversion due to esterification process is reactive equilibrium limited.
Extraction	Saha *et al.* (2000); Arpronwichanop *et al.* (2008)	Unable to achieve high conversion due to esterification process is reactive equilibrium limited.
Wet air oxidation (WAO)	Lin *et al.* (1996)	High temperature of 250 ^{o}C to maintain the pressure inside the reactor. This will cause high energy consumption to occur.
Esterification process by RDC	Arpornwichanop *et al.* (2008)	Able to achieve a conversion of around 95% with 35 % w/w acetic acid.

2.4 General esterification system

Esterification process involves the reaction between a carboxylic acids and alcohols in the present of acid catalysts. The chemical structures of carboxylic acids, alcohols and the acid catalysts affect the rate of reaction. Esters have distinct fruit like smell which have led to the use in artificial flavouring and fragrances. Esterification is a reversible process where the reactions are equilibrium reactions and thus, is required to be driven to completion according to Le Chatelier's principle.

It is known that the esterification of acetic acid with different types of alcohols have been studied by several researches in the past. This goes the same for the esterification of acrylic acid with different alcohols. The aim of this several investigators was to determine the kinetic model of each of the esterification process for the reaction of different alcohols with acetic acid and acrylic acid in the present of

homogeneous and heterogeneous catalysts. Some examples of esterification process which can be found in past literature are given in Table 2.2 below.

Table 2.2: Summary of esterification process that have been studied by past researchers.

Reactants	**Products**	**Type of catalyst used**	**Reference**
Acetic acid + isobutanol	isobutyl acetate + Water	Amberlyst IR-120 (Heterogeneous catalyst)	Altiokka and Çitak (2003)
Acrylic acid + 2-ethylhexan-1-ol	2-ethylhexyl acrylate + Water	Amberlyst-70 (Heterogeneous catalyst)	Komoń *et al.* (2013)
Acrylic acid + propylene glycol	Propylene glycol acrylate + Water	Amberlyst-15 (Heterogeneous catalyst)	Altiokka and Ödeş (2009)
Acetic acid + Butanol	Butyl acrylate + Water	Sulfuric acid (Homogeneous catalyst)	Leyes and Othmer (1945)
		Amberlyst-15 (Heterogeneous catalyst)	Gangadwala *et al.* (2003)
Acetic acid + 1-octanol	1-octyl acetate + Water	Amberlyst-36 (Heterogeneous catalyst)	Akyalçin and Altiokka (2012)
Acetic acid + propanol	Propyl acetate + Water	Dowx 50Wx8-400 (Heterogeneous catalyst)	Ali and Merchant (2006)
		Amberlite IR-120 (Heterogeneous catalyst)	
		Amberlyst-15 (Heterogeneous catalyst)	
Acetic acid + Methanol	Methyl acetate + Water	Acetic acid (Homogeneous catalyst)	Pöpken *et al.* (2000)

Reactants	Products	Type of catalyst used	Reference
Acetic acid + Methanol	Methyl acetate + Water	Amberlyst-15 (Heterogeneous catalyst)	Pöpken *et al.* (2000)

2.5 Esterification reaction to recover carboxylic acid from wastewater

According to Arpornwichanop *et al.* (2008), esterification reaction can be applied to recover carboxylic acid from wastewater by in cooperating with RDC. Through RD, the recovered carboxylic acid will be used as a reactant for the esterification process which in turn will produce a higher valued ester, save raw material cost and environmental issues concerning with the present of carboxylic acid in wastewater can be overcome. Some esterification reaction which has been applied for the recovery of carboxylic acid is shown in Table 2.3 below. Based on the table below, it can be seen that only the recovery of acetic acid through RDC has been studied by past researches up till now. Generally, it can be summarized that the overall conversion of acetic acid with different degree of dilution into acetate esters range from 67- 95 %.

Table 2.3: Summary of esterification reaction which have been applied in recovery of carboxylic acid through RDC.

Reactants	Products	Type of catalyst used	Remarks	Reference
Acetic acid + n-butanol	n-butyl acetate + Water	Amberlyst-15 (Heterogeneous catalyst)	35 % w/w Acetic acid	Arpornwichanop *et al.* (2008)
		-	30 % w/w Acetic acid	Gangadwala *et al.* (2007)
Acetic acid + 2-ethyl-1-hexanol	2-ethylhexyl acetate + Water	Amberlyst-15 (Heterogeneous catalyst)	6-15 % w/w Acetic acid	Ragaini *et al.* (2007)

Reactants	Products	Type of catalyst used	Remarks	Reference
Trifluoroacetic acid + 2-propanol	2-propyl trifluoroacetate + Water	Ion exchange resin, T-63 (Heterogeneous catalyst)	10 % w/w Trifluoroacetic acid	Mahajan *et al.* (2008)
Acetic acid + ethanol	Ethyl acetate + Water	Polystyrene-supported sulfonic acid (Heterogeneous acid)	50 % w/w Acetic acid	Yagyu *et al.* (2013)

2.6 Catalyst in esterification

2.6.1 Introduction

Basically, catalyst can be divided into homogeneous or heterogeneous. This is also applicable for reactive distillation column.

In the term of chemistry, homogeneous catalysis occurs when the catalyst is in the same phase (solid, liquid or gas) as the reactants. Homogeneous catalysis on the other hand is likely to be influenced by the changing of concentration to enhance or lower the reaction velocity (Sundmacher and Kienle, 2003, p.48). Enzymes are homogeneous catalysts which are also known as biocatalysts.

Meanwhile, heterogeneous catalysts which are practically used in the industry are in the form of solids. According to Altiokka and Çitak (2003), heterogeneous catalyst is more advantages compare to homogeneous catalyst. Heterogeneous catalyst is able to eliminate corrosive environment, can be easily remove from the reaction mixture by decantation or filtration and lastly, the purity of the products is higher compare to homogeneous catalyst since the side reactions can be completely eliminated or are less significant. Examples of heterogeneous catalysts used for esterification reaction in the recovery of carboxylic acid from wastewater are Amberlyst-15 (Arpornwichanop *et al.,* 2008; Ragaini *et al.,* 2007) and Indion 130 (Saha *et al.,* 2000).

2.6.2 Homogeneous

Strong mineral acids, such as H_2SO_4, HCl and HI, and also strong organic acids, such as HCOOH are some types of homogeneous catalysts which are being applied for the esterification of carboxylic acid (Lilja *et al.,* 2002). During the esterification reaction involving homogeneous catalyst, the slow step of the reaction involves the nucleophilic attack of the alcohol on the protonated carbonyl group of carboxylic group. According to Liu *et al.* (2006), the mechanisms route can be describe as follows:

- Firstly, protonation of the carboxylic acid takes place.
- Then, reaction with nonprotonated alcohol to yield a tetrahedral intermediate is activated.
- Finally, by decomposition, it produces the products of reaction which are ester and water.

However, there are some drawbacks towards homogeneous catalyst. According to Lilja *et al.* (2002), the miscibility of homogeneous catalyst with the reaction medium will cause difficulty in the separation between the products and reactants. Furthermore, the present of higher catalyst concentration will cause corrosion of the equipment to occur.

Even though due to the disadvantages of homogeneous catalyst which have been stated above, there are still studies being carried out by researchers on the esterification process by applying homogeneous catalyst. Lilja *et al.* (2002) have studied the esterfication of acetic, propanoic and pentanoic acid with methanol, ethanol, 1-propanol, 2-propanol, butanol and 2-butanol in the present of liquid HCl whereas Liu *et al.* (2006) have studied the esterification of acetic acid with methanol in the present of H_2SO_4.

2.6.3 Heterogeneous

Heterogeneous catalyst can be divided into three categories: solid ion exchange resins, zeolite and enzymes. According to Komoń *et al.* (2013), there are two main classes of sulfonated ion exchange resins which are popular in the industry: one is based on polystyrene/divinylbenzene matrix which includes Amberlyst and Dowex type resins and the other is based on perfluorinated sulfonic acid resins like Nafion and Aciplex.

On the other hand, as for zeolite type heterogeneous catalyst, H-ZSM-5 and NaY and VOx over USY have been stated in past literatures (Okuhara *et al.,* 1998;

Marchetti and Errazu, 2008). The NaY over USY is a base catalyst whereas the VOx over USY is an acid catalyst. Lipozyme CALB and Lipozyme T.L 100L from Novozymes are some example of enzyme based heterogeneous catalysts which have been studied by Marchetti and Errazu (2008).

Examples of heterogeneous catalysts which have been used for esterification reaction are as follows:

- Esterfication of acetic, propanoic and pentanoic acid with methanol, ethanol, 1-propanol, 2-propanol, butanol and 2-butanol in the present of fibrous polymer-supported sulphonic acid catalyst, Smopex-101 (Lilja *et al.*, 2002).
- Esterification of acetic acid with methanol on the present of Nafion/silica nanocomposite catalyst (SAC-13) (Liu *et al.*, 2006).
- Esterification of propanoic acid with n-butanol in the present of solid acid $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ in the present of excess water (Okuhara *et al.*, 1998).

2.7 Reactive distillation technology

2.7.1 Introduction

Instead of carrying out the reaction and separation process separately, it is possible to combine these operations into a single unit operation. This is called reactive distillation or catalytic distillation (Luyben and Yu, 2008, p. xvii). Reactive distillation is an excellent example of process intensification which is able to provide an economically and environmentally attractive alternative to conventional multiunit flow sheets in some systems. RDC consists of a reactive section in the middle with non-reactive rectifying and stripping sections at the top and bottom of the RDC. In the reactive column, the products are separated *in situ*, which drives the equilibrium to the product side and thus, preventing any undesired side reactions between the reactants and product which could hinders the achievements of a high conversion (Taylor and Krishna, 2000; Luyben and Yu, 2008, p.2). Figure 2.1 below shows the conventional method and the RD method of carrying out a chemical process.